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RESEARCH ARTICLE

Critical behaviour of the specific heat and the thermal expansion close to the melting point in ammonia solid III

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Abstract

A linear correlation between the specific heat C_P and the thermal expansion α_p is established here for constant temperatures close to the melting pressure in ammonia solid III. For this correlation, the experimental data for the isothermal compressibility κ_T is analysed according to a power-law formula with the critical exponent γ and, the C_P and α_p are calculated as a function of pressure near the melting point in ammonia solid III.

Values of the entropy changes with the temperature, which are extracted from linear plots of C_P against α_p, decrease as the temperature increases for the ammonia solid III prior to melting.

Keywords

Specific heat · thermal expansion · melting point · ammonia solid III.

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1 Introduction

Ammonia has three solid phases, namely, I, II and III with the different crystal structures, as determined experimentally [1]-[4]. Ammonia solid I has four molecules per unit cell in a cubic structure with the space group P_{213} [1]-[3], whereas ammonia solid II has two orientationally disordered molecules per unit cell in a hexagonal close-packed structure (hcp) with the space group P_{63}/mmc [4]. The third solid phase which exists at 35 kbar at 25 ^{o}C, has a face centered cubic (fcc) structure [5].

The Raman spectra of ammonia solid I [6] and II [7]-[10] have been obtained and the temperature dependence of the Raman frequencies for the lattice modes of solid I [6] and solid II [10] have been determined experimentally. Also, the pressure dependence of the Raman frequencies for the lattice modes has been obtained experimentally for the ammonia solid II [8]. We have calculated the Raman frequencies of two translational modes and one librational mode as a function of pressure close to the melting point in ammonia solid I [11]. For ammonia solid II, we have also calculated the Raman frequencies of a rotatory lattice (librational) mode as a function of temperature for constant pressures near the melting point in our previous study[12].

Phase diagrams containing the solid I, II and III phases of ammonia have been obtained from the experimental measurements as P-T phase diagrams [5, 8, 13] and a V-T phase diagram [6] in the literature. We have also calculated P-T phase diagram of solid I and II with the melting curves in ammonia [14] and T-P phase diagram of solid I, II and III phases [15] using the mean field theory. The experimental P-T phase diagram of ammonia [5,8], as given in Fig. 1, shows that phase III melts directly as the pressure decreases, for example, from 0,9 GPa at a constant temperature of 280K. The experimental data for the measurements of the molar volume V and the isothermal compressibility κ_T of ammonia as a function of pressure, which we analyzed in this study, were taken at constant temperatures within the P-T range where phase III solid ammonia exists [16].

Near the melting point, it has been obtained that the isothermal compressibility κ_T of ammonia exhibits a divergence behaviour [5], [16]. We have also investigated the critical behaviour of ammonia (solid I and II) near the melting point in

our earlier study [17]. By correlating the specific heat C_p with the thermal expansion α_p (first Pippard relation) and the thermal expansion α_p with the isothermal compressibility κ_T (second Pippard relation), we have established the Pippard relations in ammonia solid I and II close to the melting point [18]. We have also established the spectroscopic modification of the Pippard relation which relates the specific heat C_p to the frequency shifts $(1/\upsilon)\ (\partial\upsilon/\partial T)_P$ for the rotatory [19] and translatory [20] lattice modes in ammonia solid II near the melting point.

In high pressure research, high pressure measurements of phase properties are essential for those which undergo phase transitions. Since ammonia solid III exists at high pressures, its phase properties, in particular, thermodynamic properties should be determined. Thus, predictions for the critical behaviour of the thermodynamic quantities prior to melting in ammonia solid III, as given in this study, can be examined by the high pressure measurements performed for this crystalline system. As an application, this should be of interest to study ammonia solid III in the high pressure research work.

We study here the pressure dependence of the thermodynamic quantities such as the specific heat C_p, thermal expansion α_p and the isothermal compressibility κ_T near the melting point for ammonia solid III. Since ammonia solid III exhibits anomalous behaviour prior to melting such as ammonia I and II, it is interesting to study this material to investigate its critical behaviour. Our work given here is based on the experimental results of Pruzan et al. [16,21] for ammonia solid. Thus, the experimental data for the pressure dependence of the isothermal compressibility κ_T [16] at three constant temperatures (254.6, 274.0 and 297.5K) is analyzed according to a power-law formula and the values of the critical exponent γ for κ_T are extracted. Using the expressions for the pressure dependence of the thermal expansivity α_p and of the specific heat C_p which we have also derived in our recent study on carbon tetrachloride [22], we calculate here α_p and C_p as a function of pressure for the three constant temperatures considered near the melting point for ammonia solid III. By plotting C_p against the α_p, we examine the first Pippard relation near the melting point in ammonia solid III.

Below, we give our calculations and results for α_p and C_p close to the melting point in ammonia solid III, in section 2. We discuss our results in section 3. Finally, conclusions are given in section 4.

2 Calculations and results

The isothermal compressibility κ_T which is defined as

$$\kappa_T \equiv -(1/V)(\partial V/\partial P)_T \tag{1}$$

can be expressed as a function of pressure near the melting pressure P_m by a power-law formula,

$$\kappa_T = k(P - P_m)^{-\gamma} \tag{2}$$

where γ is the critical exponent, k is the amplitude of the isothermal compressibility. Near the melting point, variation of the melting pressure P_m with the temperature can be written approximately [16],

$$[P - P_m(T)]/[T_m(P) - T] = dP_m/dT \tag{3}$$

By means of Eq. (3), the isothermal compressibility κ_T can be written as a function of temperature

$$\kappa_T = k(dP_m/dT)^{-\gamma}\,(T_m - T)^{-\gamma} \tag{4}$$

The thermal expansion α_p which is defined as

$$\alpha_p \equiv (1/V)(\partial V/\partial T)_P \tag{5}$$

can also be expressed as functions of pressure and temperature. Using Eq. (2) in the thermodynamic relation

$$\alpha_p/\kappa_T = dP_m/dT \tag{6}$$

the thermal expansion α_p can be obtained as a function of pressure,

$$\alpha_p = k(dP_m/dT)(P - P_m)^{-\gamma} \tag{7}$$

Similarly, by using Eq. (4) in Eq. 6, the thermal expansion α_p can be obtained as a function of temperature,

$$\alpha_p = k(dP_m/dT)^{1-\gamma}\,(T_m - T)^{-\gamma} \tag{8}$$

The temperature and pressure dependencies of the specific heat C_p can also be derived from the above relations. By writing the thermodynamics relation;

$$(\partial P/\partial T)_S = C_P/(TV\alpha_p) \tag{9}$$

and approximating

$$(\partial P/\partial T)_V = dP_m/dT = (\partial P/\partial T)_S \tag{10}$$

close to the melting point for ammonia [16], the pressure dependence of the specific heat C_p can be obtained as

$$C_p = TV(P)\alpha_p(dP_m/dT) \tag{11}$$

In Eq. (11) the pressure dependence of the thermal expansion α_p is given by Eq. (7) and the volume V depends upon the pressure as

$$V(P) = V_c \exp[-k(1-\gamma)^{-1}(P - P_m)^{-1-\gamma}] \tag{12}$$

which can be derived from the definition of the isothermal compressibility Eq. (1). In Eq. (12) V_c denotes the critical volume as the critical point is close to the melting point for ammonia solid III. Similarly, the temperature dependence of the specific heat can be obtained as

$$C_p(T) = TV(T)\alpha_p(T)(dP_m/dT) \tag{13}$$

where $\alpha_p(T)$ is given by Eq. (8) and

$$V(T) = V_c \exp[-k(1-\gamma)^{-1}(dP_m/dT)^{1-\gamma}\,(T_m - T)^{1-\gamma}] \tag{14}$$

Eq. (14) can also be derived from the definition of thermal expansion Eq. (5). Finally, by knowing the temperature and pressure dependencies of the thermal expansion α_p, and the specific heat C_P, we are able to establish the Pippard relation near the melting point for ammonia solid III. This relates linearly the specific heat C_P to the thermal expansion α_p near the melting point in ammonia solid III.

As derived by Pippard on the basis of a cylindrical approximation to the form of the entropy and volume surfaces in the vicinity of the λ-point and applied to the NH_4Cl [23], we derive it for the specific heat C_P and the thermal expansion α_p of ammonia solid III near its melting point. Following Pippard [23], the entropy surface can be approximated to

$$S = S_m(P) + f(P - \Lambda T) \tag{15}$$

In a given pressure range, where $\Lambda = dP_m/dT$ is the slope of the melting line. S_m represents the entropy value at the melting temperature T_m, which varies smoothly with the pressure (contains no quadratic or higher terms [23]). Since the slope Λ is constant at the melting point, the second derivative of the entropy with respect to the temperature and pressure yields

$$(\frac{\partial^2 S}{\partial T^2})_P = \Lambda^2 f'', \quad (\frac{\partial^2 S}{\partial T \partial P}) = -\alpha f'', \quad (\frac{\partial^2 S}{\partial P^2})_T = f'' \tag{16}$$

where f'' is the second derivative of f with respect to its argument. Eq. (16) gives rise to the relation

$$\frac{\partial}{\partial T}(\frac{\partial S}{\partial T})_P = \Lambda \frac{\partial}{\partial T}(\frac{\partial V}{\partial T})_P \tag{17}$$

and

$$\frac{\partial}{\partial P}(\frac{\partial S}{\partial T})_P = \Lambda \frac{\partial}{\partial P}(\frac{\partial V}{\partial T})_P \tag{18}$$

using the thermodynamic relation

$$(\frac{\partial V}{\partial T})_P = -(\frac{\partial S}{\partial P})_T \tag{19}$$

By integrating Eq. (17) or Eq. (18) and using the definition of the specific heat

$C_P = T(\partial S/\partial T)_P$ and the thermal expansion α_p Eq. (5), we finally obtain the Pippard relation as

$$C_P = TV(dP_m/dT)\alpha_p + T(dS/dT)_m \tag{20}$$

with the slope $\Lambda = dP_m/dT$ and the integration constant $T(dS/dT)_m$. In Eq. (20), $(dS/dT)_m$ represents the variation of the entropy S with the temperature at the melting point for ammonia solid III.

In order to examine the Pippard relation Eq. (15), we started by analysing the experimental data for the isothermal compressibility κ_T as a function of pressure for the fixed temperatures at 254.6, 274 and 297.5K [16] close to the melting pressure in ammonia solid III. From our analysis, the pressure dependence of the isothermal compressibility κ_T is plotted in a log-log scale

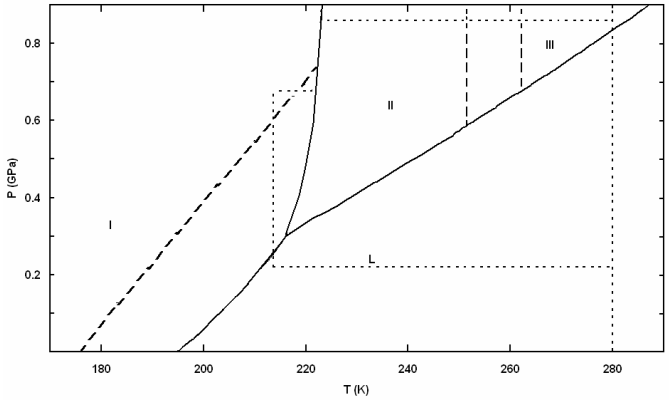

Fig. 1. Phase diagram of ammonia: ————solid lines: melting curve and transition line I-II [5]. - - - - - - - broken line: appearance of sound signal on lowering T or raising P [5]. - - - - - - thin broken line: transition zone II-III [8]. ····· dotted line: range of the previous investigation [8]. This phase diagram of ammonia is taken from Ref. [8].

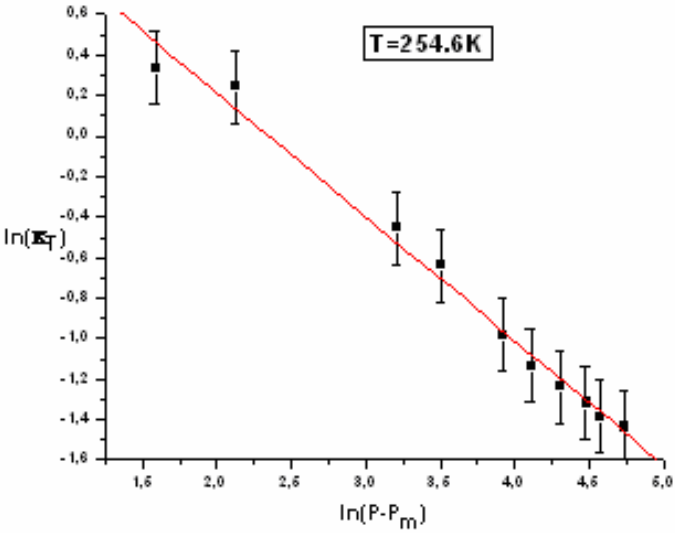

Fig. 2. A log-log plot of the isothermal compressibility κ_T as a function of P-Pm for 254.6K from the analysis of the experimental data [16] according to Eq. (2) close to the melting pressure P_m in ammonia solid III. Uncertainties in κ_T are also indicated here.

for constant temperatures at 254.6, 274 and 297.5K in Figs. (2-4), respectively. By determining the values of the critical exponent γ for κ_T and the amplitude k for the three fixed temperatures considered according to the power-law formula Eq. (2), the thermal expansion α_p and the specific heat C_P were calculated as a function of pressure by Eqs. (7) and (11), respectively. In Eq. (11) the pressure dependence of the molar volume was calculated from Eq. (12). Thus, the experimental data for the κ_T [16] was analyzed and the values of γ and k were determined using Eq. (2), as tabulated in Table 1 for fixed temperatures at 254.6, 274 and 297.5K in ammonia solid III. Using the experimental value of dPm / dT = 13 MPa / K [16], the pressure dependence of thermal expansion α_p was then evaluated by Eq. (7) with the values of γ and k for the fixed temperatures considered (Table 1) here in ammonia solid III. We also evaluated the molar volume at various pressures in the same pressure interval for the analysis for the fixed temperatures at 254.6, 274 and 297.5K

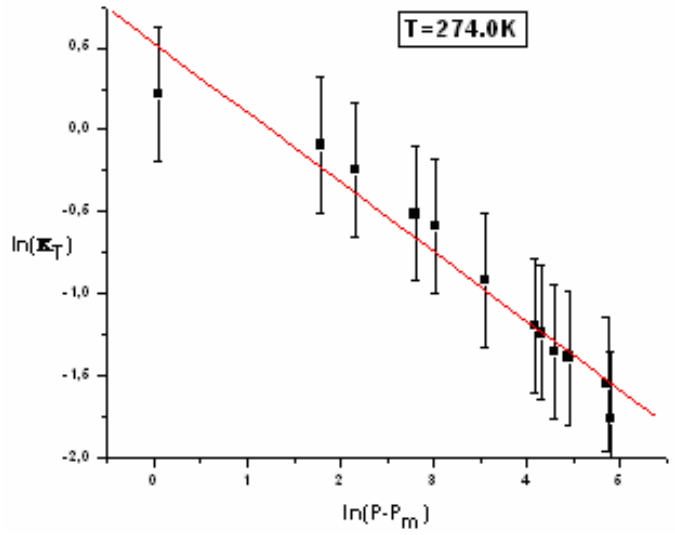

Fig. 3. A log-log plot of the isothermal compressibility κ_T as a function of $P - P_m$ for 274K from the analysis of the experimental data [16] according to Eq. (2) close to the melting pressure P_m in ammonia solid III. Uncertainties in κ_T are also indicated here.

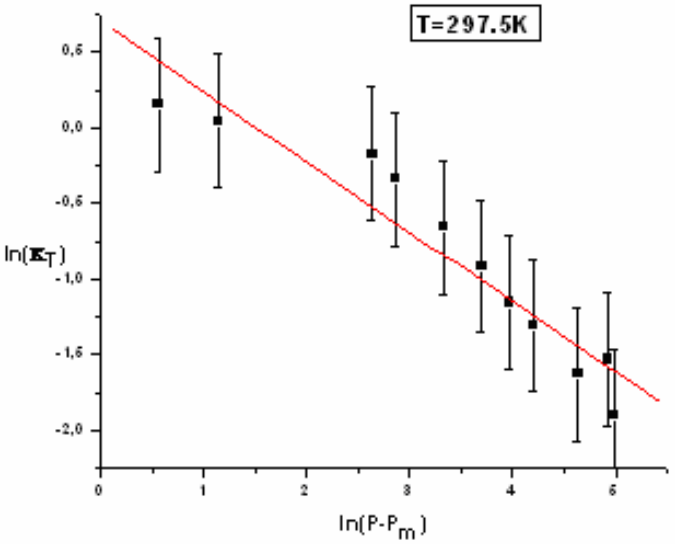

Fig. 4. A log-log plot of the isothermal compressibility κ_T as a function of $P - P_m$ for 297.5K from the analysis of the experimental data [16] according to Eq. (2) close to the melting pressure P_m in ammonia solid III. Uncertainties in κ_T are also indicated here.

close to the melting point in ammonia solid III, according to Eq. (12). Therefore, the pressure dependence of specific heat C_P was calculated by knowing the pressure dependence of the thermal expansion α_p and the volume V for constant temperatures at 254.6, 274 and 297.5K, according to Eq. (11) in ammonia solid III.

Since we obtained the pressure dependence of the specific heat C_P and thermal expansion α_p at constant temperatures studied, we then plotted C_P against α_p according to the Pippard relation (Eq. (15)). Our plots for the constant temperatures at 254.6, 274 and 297.5K close to the melting point in ammonia solid III, are given in Figs. 5-7, respectively. In Table 1, we give the values of the intercept $(dS/dT)_m$ at the melting point, which we extracted from our plots (Figs. 5-7 according to Eq. (15).

3 Discussion

The specific heat C_P and the thermal expansion α_p which we calculated here at various pressures vary linearly, as plotted in Figs. 5-7 for constant temperatures at 254.6, 274 and 297.5K, respectively close to the melting in ammonia solid III. This linear variation of the specific heat C_P with the thermal expansion α_p indicates that both thermodynamic functions exhibit similar critical behaviour near the melting point in ammonia solid III. According to the γ values (Table 1) the critical behaviour of C_P and α_p is closer for constant temperatures at 274K (Fig. 6) and 297.5K (Fig. 7). The experimental uncertainties from the measurements of the isothermal compressibility κ_T as a function of pressure, which was considered in our analysis given here (Figs. 2-4), also occur as uncertainties in the thermal expansion α_p and in the specific heat C_P. When the specific heat C_p is plotted against α_p by considering uncertainties in both functions, a linear variation for constant temperatures at 254.6, 274 and 297.5K does not vary significantly, as shown in Figs. 5-7), respectively with the same slope of $dP_m/dT = 13$MPa/K. Considering the exponent values that vary from 0.4 to 0.6 (Table 1), ammonia solid III exhibits a second-order phase transformation prior to melting, as suggested for ammonia solids I and II [16]. The second-order transition in ammonia proceeds up to first-order melting [16]. This transformation may be due to an orientational disorder [21]. So that the specific heat C_P and the thermal expansion α_p show anomalous behaviour near the melting point, which can be related to the orientational motion of NH_3 molecules in the ammonia solid III. The reorientation of NH_3 molecules is in fact due to the progressive breaking of the weak hydrogen bonds in ammonia solid III. This breaking of hydrogen bonds may account for a dramatic softening of solid ammonia on approach to melting [21]. Thus, the hydrogen bond distortion can occur by thermal motion near the melting point in ammonia solid III. At a constant pressure, the orientational disorder in ammonia solid III decreases as the temperature increases near the melting point (Fig. 1). The orientational disorder contributes to instability of the ammonia solid III, which causes anomalies in the specific heat C_P, thermal expansion α_p and the isothermal compressibility κ_T prior to melting in this crystalline system.

From linear variation of the specific heat C_P with the thermal expansion α_p, variation of C_P with the pressure can be calculated according to the thermodynamic relation

$$\partial C_P/\partial P = VT(\alpha_p^2 + \partial\alpha_p/\partial T) \qquad (21)$$

for ammonia solid III. This can also examine the critical behaviour of C_P and α_p close to the melting point in ammonia solid III.

Tab. 1. Values of the critical exponent γ for the isothermal compressibility κ_T and the amplitude k from the analysis of the experimental data [16] according to Eq. (2) and the values of the intercept $(dS/dT)_m$ extracted from Eq. (20) at the melting point for fixed temperatures indicated in the pressure range close to the melting point in ammonia solid III. Uncertainties in γ and $\ln k$ are also given here.

$T(K)$	γ	$\ln k$	$P - P_m(MPa)$	$(dS/dT)_m$ $(J/mol.K^2)$
254.6	0.61 ± 0.02	1.44 ± 0.09	$4.9 < P - P_m < 114.3$	2.47×10^{-2}
274.0	0.42 ± 0.03	0.53 ± 0.11	$1.1 < P - P_m < 132.9$	-3.65×10^{-4}
297.5	0.46 ± 0.05	0.70 ± 0.18	$1.7 < P - P_m < 146.5$	-2.0×10^{-2}

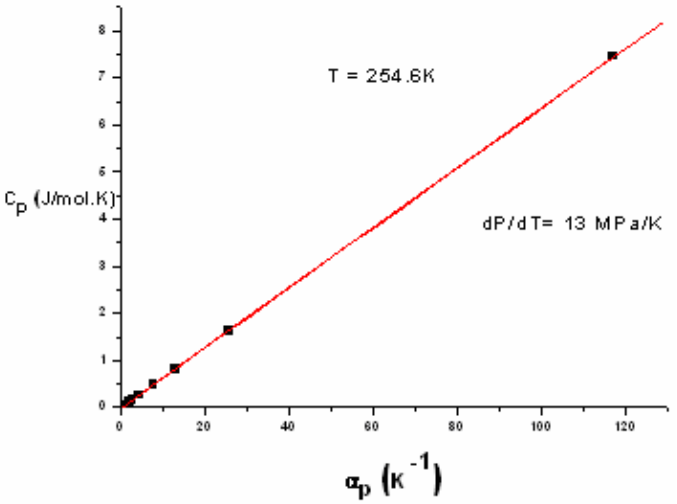

Fig. 5. The specific heat C_P as a function of thermal expansion α_p for 254.6K, according to Eq. (20) close to the melting pressure P_m in ammonia solid III.

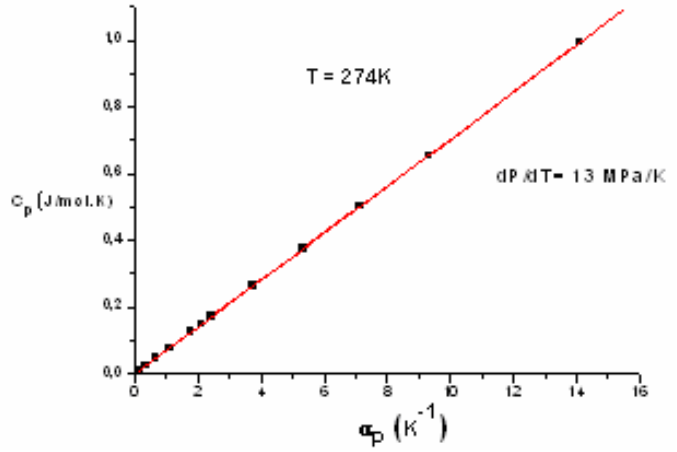

Fig. 6. The specific heat C_P as a function of thermal expansion α_p for 274K, according to Eq. (20) close to the melting pressure P_m in ammonia solid III.

4 Conclusions

The specific heat C_P was related to the thermal expansion α_p close to the melting pressure for constant temperatures at 254.6, 274 and 297.5K in ammonia solid III. A linear variation of C_P with α_p was obtained here by analyzing the experimental data for the isothermal compressibility κ_T near the melting point in this solid system. The exponent values deduced from the analysis of the κ_T indicate that ammonia solid III undergoes a second order phase transformation prior to melting, as suggested for the ammonia solids I and II, previously. Also, a linear variation of C_P with α_p is an indicative of similar critical behaviour of both

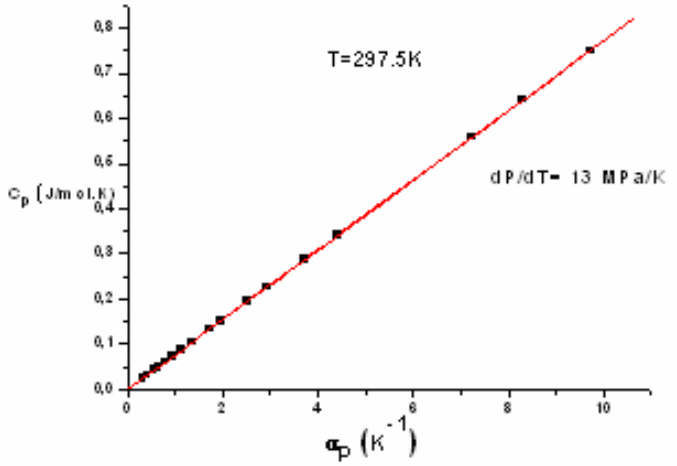

Fig. 7. The specific heat C_P as a function of thermal expansion α_p for 297.5K , according to Eq. (20) close to the melting pressure P_m in ammonia solid III.

thermodynamic quantities which can be examined by the experimental measurements close to the melting point in ammonia solid III.

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